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PREPARATION OF Cu_xS THIN FILMS BY ACTIVATED REACTIVE EVAPORATION TECHNIQUE

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Thin films of cuprous sulphide (Cu_2S) have been deposited for the first time by a novel Activated Reactive Evaporation (ARE) technique. These films have been deposited as a function of various deposition conditions such as partial pressure of hydrogen sulphide gas, substrate temperature and copper evaporation rate. The microstructure of the films have been characterized by optical microscopy, transmission electron microscopy and electron diffraction. Electrical and optical characterization has also been carried out. Films deposited using, a H_2S partial pressure in the range from 10^{-2} to 8×10^{-4} Torr, a substrate temperature at or near room temperature and a copper evaporation rate of about 200 Å/min, were found to consist of pure chalcocite (Cu_2S). Electrical and optical measurements of the pure Cu_2S films indicated that these films were p-type with carrier concentrations of $1\text{–}7 \times 10^{20}/cm^3$ and typical mobility values of 1–3 cm^2/V s. Mobilities as high as 8 cm^2/v s were measured on some samples. The optical determination of the band gap gave a value of $E_g \approx 1.2$ eV. Preliminary investigation of the Cu_2S/CdS heterojunctions were also carried out using ARE deposited Cu_2S films on CdS films prepared by direct evaporation.

1. Introduction

Thin film Cu_2S/CdS solar cells have demonstrated an efficiency of around 10% [1]. The active layer in these cells is the chalcocite (Cu_2S) film. Although the most efficient Cu_2S/CdS solar cells produced to date have been obtained using Cu_2S films obtained by the chemiplating technique [1] alternative methods have been searched for the production of stoichiometric Cu_2S films. Several workers have reported on the preparation of Cu_2S films by vacuum deposition techniques such as sputtering [2, 4] and direct evaporation [5, 6]. In the present investigation, we report for the first time on the use of the Activated Reactive Evaporation (ARE) technique [7] for the deposition of Cu_2S films. The ARE process is a plasma-assisted deposition process in which Cu atoms from a resistance heated evaporation source react with H_2S gas molecules to deposit the Cu_xS films, the process being activated by the presence of a plasma. This process would permit the fabrication of solar cells in a sequential all vacuum process.

2. Experimental details

The films were prepared in an 18 in. (46 cm) vacuum system – consisting of an oil diffusion pump and mechanical pump capable of achieving a vacuum of $\approx 10^{-6}$ Torr. The system was equipped with an electron emitter and an anode assembly. The H_2S gas was bled into the system by a calibrated leak valve. The plasma was generated by applying a positive dc potential of about 120 V to the anode and heating the electron emitter to generate electrons by thermionic emission. Magnetic field coils were used to confine the plasma and enhance the reaction. A schematic of the experimental set up is shown in fig. 1.

The system was pumped down to 5×10^{-6} Torr before each run. A resistively heated molybdenum boat was used to evaporate copper metal. The substrate and source temperatures were monitored using Chromel–Alumel thermocouples. Film characterization was done using transmission electron microscopy, electron diffraction, optical transmittance and Hall effect measurements. A Carry 14 spectrophotometer was used in transmission measurements. Scattering effects were ignored due to the general increase in transmission with decreasing wavelength. The stoichiometry of the films was inferred from the phases present in the films.

3. Results and discussion

The structure and the various electron transport and optical properties of Cu_2S films depend sensitively on the deposition conditions. The effects of various deposition parameters are described below.

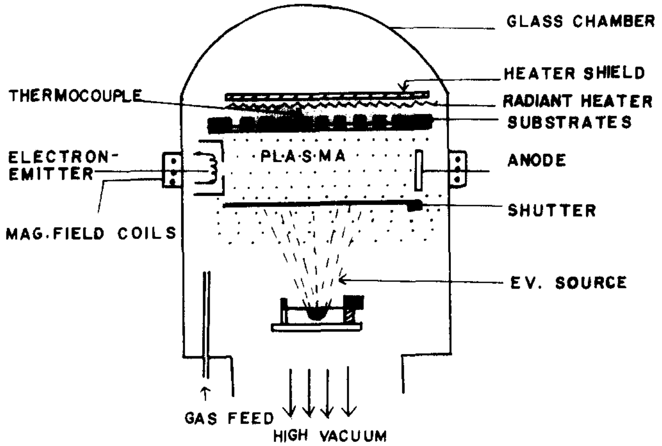


Fig. 1. Schematic of experimental set-up for deposition of Cu_xS films by ARE.

3.1. H_2S partial pressure (p_{H_2S})

H_2S partial pressure was varied from 2×10^{-4} to 10^{-2} Torr, keeping the substrate temperature and the source temperature (copper evaporation rate) constant. Two different substrate temperatures were chosen. The first corresponded to approximately room temperature. There was no intentional heating of the substrate except for the radiative heat from the boat which raised the temperature to $\approx 40°C$ by the end of the run. The second substrate temperature chosen was 200°C. The source temperature was fixed at 1250°C in both cases. At this source temperature the arrival rate of Cu at the substrate was found to be 200 Å/min. This was determined by measuring the film thickness produced by evaporating Cu in an equivalent partial pressure of argon for a fixed time. The variation of the electrical resistivity of Cu_xS films as a function of pH_2S is shown in fig. 2. Curve A is for $T_{sub} \approx 25°C$ and curve B is for $T_{sub} = 200°C$. The films deposited at room temperature (25°C) and using p_{H_2S} in the range 8×10^{-4}–10^{-2} Torr had an electrical resistivity around 10^{-2} Ω cm and they were found to consist of single phase chalcocite (Cu_2S) as shown by electron diffraction and transmission electron microscopy observations. A typical electron diffraction and an electron

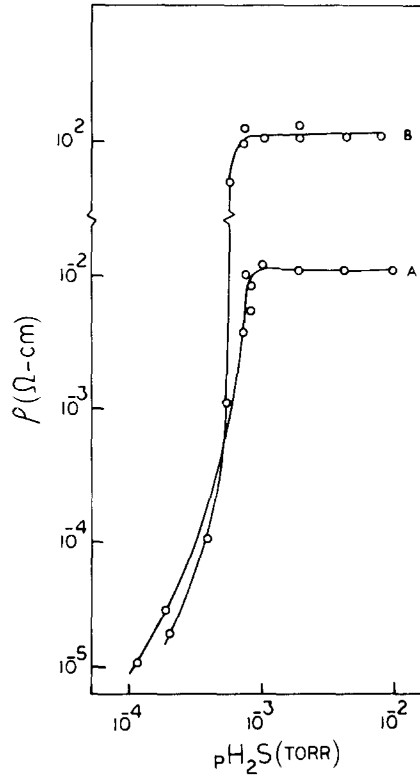
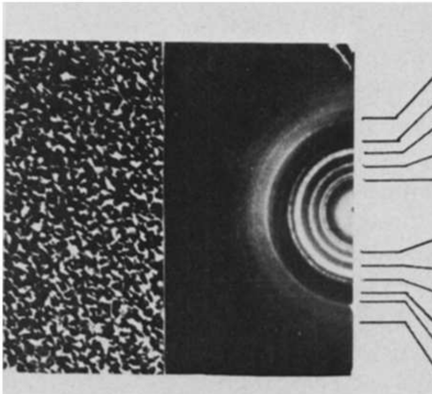


Fig. 2. Variation of the electrical resistivity of Cu_xS films as a function of H_2S partial pressure. $T_s = 1250°C$, $T_{sub} \approx 25°C$ (A), $T_{sub} = 200°C$ (B).



dÅ	hkℓ	INTENSITY
1.27	-----	MEDIUM
1.69	604, 0160	MEDIUM
1.95	600	STRONG
2.57	304	MEDIUM
3.36	340, 080	WEAK
3.01	342, 082	MEDIUM
2.14	012	WEAK
1.87	312, 0124	STRONG
1.51	684, 644	WEAK
1.35	-----	WEAK
1.11	-----	WEAK

Fig. 3. Electron diffraction pattern and electron micrograph of the single phase Cu_2S film.

micrograph are shown in fig. 3. These films had a grain size of about 300 Å. Hall measurements made on 3000–5000 Å thick films showed the films to be p-type with mobilities in the range of 1–3 $cm^2/V\ s$. A few samples showed even higher mobilities (8 $cm^2/V\ s$). Of course these mobility values should not be taken as bulk values; they are characteristic of thin films.

The highest mobility values were obtained for films deposited at $\sim 10^{-3}$ Torr p_{H_2S}. The reasons for the shape of curve B will be explained in section 3.2. However, it should be noted that the low resistivity chalcocite films obtained at low substrate temperatures are near-stoichoimetric films. It will be shown in the later sections that the resistivity increases sharply as x in Cu_xS approaches 2. Similar results were reported by Jonath et al. [4] for Cu_2S films deposited using magnetron reactive sputtering. These authors have also observed two types of copper sulphide depending on the deposition conditions. One type of material which formed primarily on substrate at 130°C, exhibited a resistivity of $\sim 10^2\ \Omega$ cm and a high density of Cu nodules on the surface. The second type of material, which formed primarily at low substrate temperatures (35°C), exhibited low resistivity ($\approx 10^{-2}\ \Omega$ cm) and much lower density of Cu nodules. However, in the present investigations using ARE technique, no Cu nodules were observed in low resistivity Cu_2S films.

3.2. *Substrate temperature* (T_{sub})

The substrate temperature was varied from 25 to 320°C, keeping the source temperature fixed at 1250°C and using $p_{H_2S} \approx 10^{-3}$ Torr. Fig. 4 shows the variation of the electrical resistivity of as-deposited films as a function of the substrate temperature. The films deposited at substrate temperatures up to 100°C were found to be single phase Cu_2S, similar to the films described in the previous section. However, as the substrate temperature was increased above 100°C the resistivity of the films was first found to decrease and then increase sharply above 175°C. The reason for this behavior

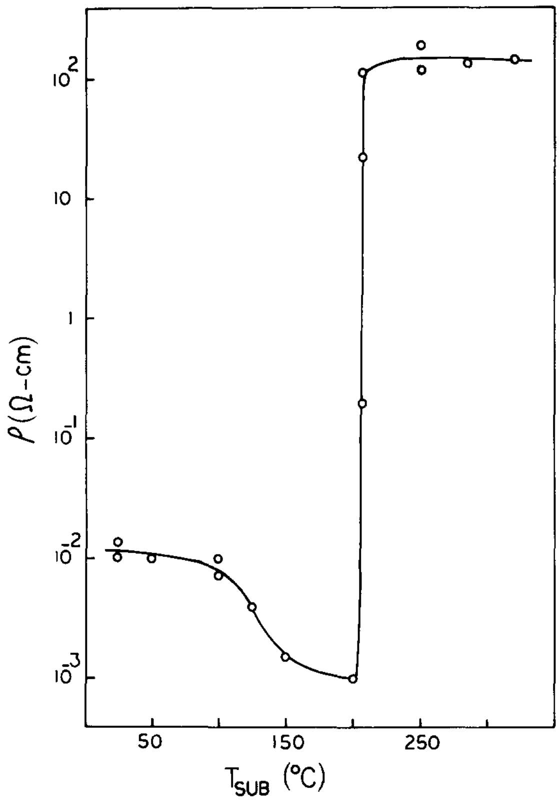


Fig. 4. Variation of the electrical resistivity of Cu_xS films as a function of substrate temperature, $T_s = 1250°C$, $p_{H_2S} \approx 10^{-3}$ Torr.

can be explained using the phase diagram shown in fig. 5 [4]. From this diagram, one can observe that if the composition of the deposited film were slightly to the left of the $x = 2$ line, the film would be the pure chalcocite phase at low temperatures. As the temperature increases, one could cross the boundary into the chalcocite plus digenite region. Because of the lower resistivity of digenite, the overall resistivity of the mixed phase films would decrease with increasing digenite concentration, resulting from increasing temperature. This observation receives further support from the fact that these films were found to contain the digenite phase as confirmed by electron diffraction and optical transmittance spectra.

However, as the substrate temperature is further increased, one would expect two things to happen (i) increased re-evaporation of sulphur from the substrates and (ii) increased adatom mobility.

The former would tend to make the films copper rich whereas the latter would give rise to enhanced reactivity to form Cu_2S phase. These films were found to consist of two phases and electrical resistivity rose very sharply to a level of $\approx 10^2$ Ω cm. The two phases were identified as a Cu_2S matrix with Cu nodules. A typical electron

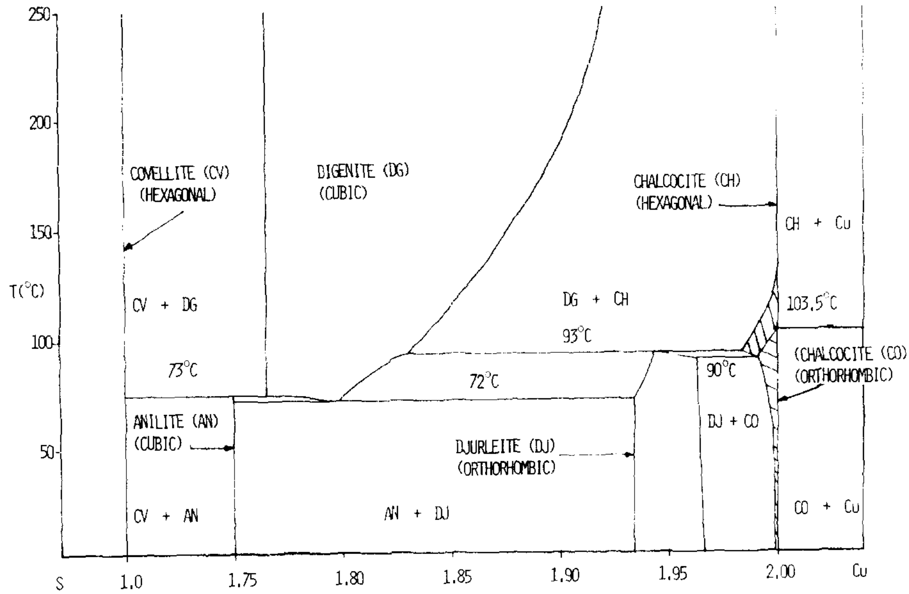


Fig. 5. Phase diagram of the Cu–S system [3].

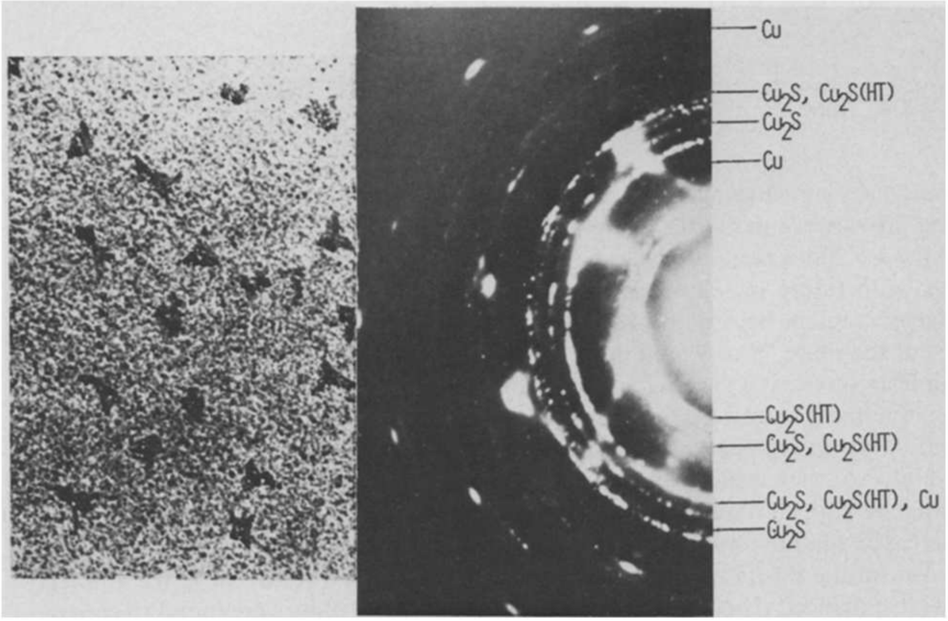


Fig. 6. Electron micrograph and electron diffraction pattern of a film deposited at $p_{H_2S} \simeq 9 \times 10^{-4}$ Torr. $T_{sub} = 250°C$, $T_s = 1250°C$.

diffraction pattern and a transmission electron micrograph for these high resistivity films are shown in fig. 6.

Similar results were observed when the electrical resistivity variation as a function of p_{H_2S} was studied at substrate temperatures of 200°C, (curve B in fig. 2).

The transmission spectra of the high resistivity films indicated a band gap value of 1.2 eV. The overall transmission in the infrared, however, was less than the transmission for lower resistivity (10^{-2} Ω cm) chalcocite films. This can be due to the blocking effect of the Cu nodules because a large density of nodulus was observable with optical microscope in transmission.

3.3. *Source temperature/Cu evaporation rate* (T_s)

The effect of Cu evaporation rate was investigated by varying the source temperature. The source temperature was varied in the range 1100–1350°C, keeping p_{H_2S} at 10^{-3} Torr and the substrate temperature at ≈50°C. The variation of the electrical resistivity in these films as a function of source temperature is shown in fig. 7.

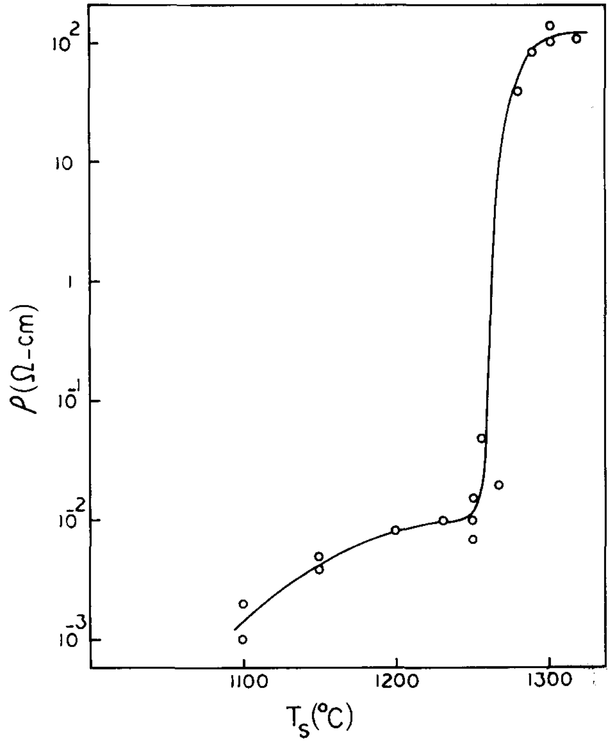


Fig. 7. Variation of the electrical resistivity of Cu_xS films as a function of source temperature, $T_{sub} = 50°C$, $p_{H_2S} \approx 9 \times 10^{-4}$ Torr.

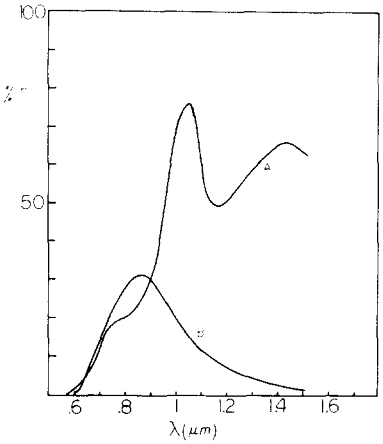


Fig. 8. Transmission spectra of Cu_xS films, curve A for Cu_2S, curve B for mixed lower phases.

The films deposited at low Cu evaporation rates (source temperature $<1200°C$) were found to be Cu deficient and yielded electrical resistivities in the range of 10^{-3}–10^{-2} cm. A mixture of Cu_xS phases were present in these films. The resistivity leveled off to that of near stoichiometric Cu_2S (10^{-2} Ω cm) at 1225°C. However, further increase in source temperature ($T_s > 1250°C$) resulted in high resistivity ($\approx 10^2$ Ω cm) films. These high resistivity films were found to consist of two phase structures similar to the ones reported in the earlier sections.

The transmittance spectra of these films showed a marked variation with the deposition conditions. Typical transmittance curves are given in fig. 8. Curve A is for a chalcocite film with electrical resistivity of $\approx 10^{-2}$ Ω cm. Curve B is for a film which had a mixture of phases and a resistivity of $\approx 10^{-3}$ Ω cm. It is observed that the band gap of the chalcocite film is ≈ 1.2 eV and infrared transmission is rather good. The transmission curve for the mixed film on the other hand is shifted to lower wavelengths which indicates a higher optical band gap. The infrared transmission for the mixed film is very low due to the free carrier absorption mechanism.

3.4. *CdS/Cu_2S heterojunctions*

Preliminary studies were made on the CdS/Cu_2S photovoltaic cells using ARE deposited Cu_2S on CdS films obtained by direct evaporation. The CdS films used for this purpose had an electrical resistivity in the range of 1–10 Ω cm. These cells had efficiencies in the order 1.2% with $V_{oc}=0.34$ V, $J_{sc}=9.5$ mA/cm², FF$=0.32$ under 85 mW/cm² illumination.

4. Conclusions

In conclusion we have shown that Cu_xS films with controlled stoichiometry phases can be prepared by the ARE technique. These films with further optimization would be applicable to CdS/Cu_2S photovoltaic device production.

Acknowledgements

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